The specification is amended to correct typographical errors and more clearly describe the invention. As the amendments are consistent with the rest of the specification (see, for example page 5, line 19, and page 7, lines 21-24), no new matter is added.

REJECTIONS UNDER 35 USC §102(b)

2. **CLAIMS 1 - 24:**

Examiner rejected Claims 1-24 under 35 U.S.C. §102(b) as anticipated by JP 2-050966, Hisamune. Examiner states

> *Hisamune clearly teaches applicant's invention (see Purpose and Constitution). Because the process is identical, including using the same source gases illuminated by a mercury lamp, the atomic concentration of oxygen would inherently be increased. However, applicant is advised that as written, the claim does not necessarily require any such increase because only the intention of increasing the atomic oxygen is claimed. Further, Hisamune teaches a deposition temperature of about 400° C and applicant claims about 480°C. Temperatures about 400° C, such as 440°C, would also be about 480°C. Therefore, the Hisamune reference anticipates applicant's deposition temperature.*
>
> *However, if it is somehow seen that applicant's deposition temperature is not anticipated, then this would be a difference.*
>
> *It has been held that optimization of parameters is obvious (see In re Aller 105 USPQ 233 (CCPA 1955)).*
>
> *Therefore, it would have been obvious to choose the temperature of applicant's claimed process because Hisamune teaches temperatures near applicant's and to provide an efficient deposition process which provides a quality silicon oxide film, according to the precedent set by In re Aller.*

Claims 1, 23, and 24 have been amended to include "optically exciting the volume of gas located within a chemically reactive distance of the substrate assembly, without exposing the substrate assembly surface to the optical excitation." Support for the amendment can be found throughout the specification in the general and repeated mention of such concepts as reducing

fixed charge and exposing only the reactive volume of gases to a source of high intensity light without the need to illuminate the substrate, and more specifically on page 7, lines 15 - 26. Applicant believes the claims are now allowable because they have been amended to more clearly describe the invention and point out a feature not found in the art.

Applicant respectfully submits that the Examiner's rejection is not well taken as the Examiner has failed to establish a prima facie case of anticipation under 35 U.S.C. §102(b). The factual determination of anticipation requires the disclosure in a single reference of every element of the claimed invention. Please refer to Ex parte LEVY, 17 USPQ.2d 1461 (1990), which cites numerous cases supporting this position. *Levy* also states that "it is incumbent upon the examiner to identify wherein each and every facet of the claimed invention is disclosed in the applied reference."

Claims 1, 23, and 24, as amended, recite optically exciting the volume of gas located within a chemically reactive distance of the substrate assembly, without exposing the substrate assembly surface to the optical excitation. Hisamune makes no reference to optically exciting or illuminating the reaction volume of gases within a chemically reactive distance of the substrate Applicant respectfully disagrees with Examiner that "*Hisamune clearly teaches applicant's invention,*" and that the *"the process is identical."* The Hisamune patent teaches irradiating the inside of the reaction chamber through a light irradiation window (see, for example, Constitution lines 8-9 and translation, page 1, lines 23 - 24). The invention, as taught and shown in the drawings in Hisamune (JP 2-050966), irradiates all of the gas in the chamber and the sample (substrate). This can be seen clearly in the figure; light irradiation window 106 constitutes the majority of the top of the chamber 101. Hisamune makes absolutely no mention of reducing fixed charge in CVD ozone deposited films or illuminating, with a source of high

intensity light, the volume of gas located within a chemically reactive distance of the substrate **without** illuminating the substrate. That is to say, illuminating the reaction volume of gas in such a manner that the substrate is not illuminated. Applicant's invention is directed to just such a method of exposing to a source of high intensity light the volume of gas located within a chemically reactive distance of the substrate surface, without exposing the substrate assembly to the light source.

The distinction between Applicant's invention and that of Hisamune is more clearly evident with the amended Claims 1, 23 and 24, as well as the claims that depend from the amended Claims 1, 23, and 24.

REJECTIONS UNDER 35 USC §103(a)

3. **CLAIMS 1 - 24:**

Examiner, in the alternative rejects Claims 1 - 24 as under 35 U.S.C. §103(a) over JP 2-050966 (Hisamune), by virtue of the same arguments as Examiner's rejections based on anticipation of the invention. It is respectfully submitted that Examiner's rejection is again not well taken, as the Examiner has failed to establish a *prima facie* case of obviousness under 35 U.S.C. §103(a). A rejection under 35 U.S.C. §103 is not proper where the PTO fails to meet the initial burden of presenting a *prima facie* case of obviousness. In re RIJCKAERT 9 F.3rd 1531,(Fed. Cir. 1993) and In re GEIGER 815 F.2d 686, 2 USPQ.2d 1276 (Fed. Cir. 1987).

The test of obviousness under 35 U.S.C. §103 requires that one compare the claimed subject matter *as a whole* with the prior art to which the subject matter pertains. See, for example, In re OCHIAI, 37 USPQ. 1127 (Fed. Cir. 1995) and In re BROUWER, 77 F.3d 422 (Fed. Cir. 1996).

The *prima facie* case requires that there must be a reason for one skilled in the art to take the cited reference and change it to reach the invention of Applicant.

Applicant finds nothing in Hisamune relating to the reasons the reference is applied by Examiner or **elsewhere in the reference** that suggests, motivates or makes possible Applicant's invention. Examiner's rejections are improper and do not meet the requirements for establishing a *prima facie* case of obviousness under 35 U.S.C. §103.

"*The mere fact that the prior art may be modified in the manner suggested by the Examiner does not make the modification obvious* ***unless the prior art suggested the desirability of the modification*** (emphasis added)." *IN RE FRITCH, 972 F.2d 1260, 23 USPQ 2d 1780 (Fed. Cir. 1992).*
(See also In re OCHIAI, 37 USPQ 1127 (Fed. Cir. 1995) and In re BROUWER, 77 F.3d 422 (Fed. Cir. 1996), both quoting IN RE GORDON. 221 USPQ 1125 (Fed. Cir. 1984)).

> *Obviousness cannot be established by combining the teaching of the prior art to produce the claimed invention, absent some teaching or suggestion supporting the combination. Under section 103, teachings of references can be combined only if there is some suggestion or incentive to do so. The prior art of record fails to provide any such suggestion or incentive. ACS Hospital Systems, Inc. v. Montefiore Hospital,* 732 F.2d 1572, 221 USPQ 929 (Fed. Cir. 1984).

Hisamune (JP 2-050966) is directed to irradiating all of the gas and the samples (substrates) in the reaction chamber, for dense film deposition, with high humidity resistance (see Constitution, lines 9 - 12 and translation, page 3, lines 33). Hisamune is completely silent on reducing fixed charge in CVD ozone deposited films or illuminating, with a source of high intensity light, the volume of gas located within a chemically reactive distance of the substrate **without**

illuminating the substrate, to accomplish reducing fixed charge is CVD ozone deposited films, as set forth by Applicant and Hisamune in no way suggests such a method.

Examiner has failed in his burden to show that applicant's invention *"as a whole,"* as laid out in 35 U.S.C. §103 is in any way suggested by the cited reference of Hisamune.

For all of the above reasons Claims 1 - 24 are patentable over the cited references and 35 U.S.C. §103 rejections.

NEW CLAIMS 25 - 30

4. New Claims 25 - 30, recite the features of reducing fixed charge in CVD ozone deposited films by optically exciting the volume of gas located within a chemically reactive distance of the substrate assembly, without exposing the substrate assembly surface to the optical excitation. Support for this language in these claims, can be found throughout the specification in the general and repeated mention of such concepts as reducing fixed charge and exposing only the reactive volume of gases to a source of high intensity light without the need to illuminate the substrate. The cited reference does not in anyway allude to a method for reducing fixed charge in CVD deposited film, nor to illuminating, with a source of high intensity light, the volume of gas located within a chemically reactive distance of the substrate **without** illuminating the substrate. The prior art also makes absolutely no mention of, nor suggests the desirability of dispensing the liquid as a fine mist, nor to decreasing the amount of liquid necessary to satisfactorily cover the substrate. Applicant's invention is directed to just such methods and concepts.

In view of the above, it is submitted that the claims are in condition for allowance. Reconsideration and withdrawal of the rejections and objections is respectfully requested. Allowance of the claims at an early date is solicited. If the Examiner feels it would advance the application to allowance, he is invited to telephone or fax the undersigned at the numbers given below.

Respectfully Submitted,

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54. Title of Invention: Method for The Manufacture of Semiconductor Device

21. Application No.: Showa 63-200489

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Specification

1. Title of the Invention

METHOD FOR THE MANUFACTURE OF SEMICONDUCTOR DEVICE

2. Patent Claim

A method for the manufacture of a semiconductor device comprising a process of chemical vapor deposition of an insulating film on the surface of a substrate placed into a reaction furnace by introducing gaseous starting materials and ozone (O_3) into said reaction furnace, irradiating the inside of said reaction furnace with ultraviolet radiation, and conducting a photochemical reaction of said gaseous starting materials and ozone.

3. Detailed Explanation of the Invention

[Field of Industrial Application]

[1] ILS Note - We were unable to verify the correct reading of this person's name. The nature of the Japanese language is such that Kanji (Chinese Characters) assigned to personal names may have multiple readings. Our best guess is provided. An alternative way of reading this name is Susumu.

EXHIBIT A

The present invention relates to a method for the manufacture of a semiconductor device. More specifically, the present invention relates to a method for forming an insulating film, such as a silicon oxide film and silicon oxide nitride film, suitable as a surface protecting film or insulating film formed between the layers of a multilayer wiring structure in semiconductor integrated circuits.

[Prior Art Technology]

Miniaturization of semiconductor integrated circuits and increase in the degree of their integration made it necessary to decrease temperature and losses in the process for the manufacture of semiconductors. A method for forming a thin film on a substrate by irradiating reaction gases with ultraviolet radiation to photo-decompose the reaction gases has been developed as one of the methods for forming in insulating film on a semiconductor substrate or between the layers in semiconductor integrated circuits in which a multilayer metal wiring structure is formed on a semiconductor substrate, and this method was suitable for forming the film without damaging the substrate and at a low temperature. Such a method is referred to as a photochemical vapor deposition method (photo-CVD). For example, a silicon nitride film can be formed by using monosilane (SiH_4) and ammonia (NH_3) as reaction gases. Furthermore, a silicon oxide film (SiO_2) can be obtained by using monosilane and oxygen (O_2) as the reaction gases (see, for example, Proceedings of the 30th Symposium on the Technology of Semiconductor Integrated Circuits, July, 1986, p. 111-116).

Furthermore, another method for forming an insulating film without damaging the substrate and at a low temperature comprises forming a SiO_2 film by using chemical vapor deposition (CVD), in which SiH_4 or tetraethoxysilane (TEOS : $Si(OC_2H_5)_4$) was reacted with ozone (O_3) (for example, Denki Kagaku, v. 45, p. 654-659, 1977).

[Problems to Be Solved by the Invention]

However, the disadvantage of the above-mentioned methods for forming insulating films by photo-CVD was that the output of a lamp (for example, a low- or high-pressure mercury lamp) used as a light source usually was small and the efficiency of photo-decomposition of the reaction gases was low. As a result, the deposition rate was low and unsuitable for industrial-scale manufacturing. For example, when a silicon nitride (SiN) film was deposited by using SiH_4 and NH_3 as starting materials, the maximum deposition rate at a temperature of 200-400°C was about 10 nm/min. When SiH_4 and O_3 were used as starting materials to deposit a SiO_2 film, the maximum deposition rate was about 25 nm/min. In other words, these methods had a very low deposition rates. Furthermore, in the CVD method for forming a SiO_2 film by decomposition of SiH_4 or TEOS with O_3, the deposition reaction proceeds only due to pyrolysis. Consequently, the deposited SiO_2 film has a compactness and moisture resistance, lower than those of the film obtained by the photo-CVD method, in which a photochemical reaction also contributes to the deposition reaction. Thus, the comparison of SiO_2 films formed at a temperature of 300°C demonstrated that the SiO_2 film formed by the photo-CVD method using SiH_4 and O_2 as starting materials had a density of 2.24 g/cm^3 and an etching rate (1% hydrofluoric acid) of 8 nm/min, whereas the SiO_2 film chemically vapor deposited by decomposing TEOS with O_3 had a density of 2.18 g/cm^3 and an etching rate (1% hydrofluoric acid) of 64 nm/min. Thus, the SiO_2 film, prepared by chemical vapor deposition using decomposition of TEOS with O_3, had a compactness much lower than that of the film obtained by photo-CVD.

[Means to Solve the Problems]

The method for the manufacture of a semiconductor device in accordance with the present invention comprises a process of chemical vapor deposition of an insulating film on the surface of a substrate placed into a reaction furnace, by introducing a gaseous starting material and ozone into the reaction furnace and irradiating the inside of the reaction furnace with ultraviolet radiation to induce a photochemical reaction of the gaseous starting material and ozone. Furthermore, it is preferred that a chemical vapor deposition apparatus be used for the implementation of this method for forming a thin film, this apparatus comprising a light source emitting ultraviolet radiation and an ozone generator for ozone generation and also having a window provided in the wall of the reaction furnace for introducing ultraviolet radiation into the reaction furnace.

[Embodiment]

The present invention will be explained below with reference to the drawings attached.

Figure 1 is a schematic diagram of the chemical vapor deposition apparatus used for explaining an embodiment of the present invention. In this figure, 101 stands for a reaction furnace, 102 stands for a sample, 103 stands for a susceptor for the sample 102, 104 stands for a heater for heating the sample 102, 105 stands for a low-pressure mercury lamp which is a light source, 106 stands for a light irradiation window made of synthetic quartz and designed to introduce ultraviolet radiation from the low-pressure mercury lamp 105 into the reaction furnace 101, 107 stands for an inlet tube for the reaction gas, and 108 stands for a discharge tube for the reaction gas. Furthermore, 109 stands for a tube for supplying gaseous oxygen, 110 stands for a tube for supplying gaseous nitrogen, 111 stands for a valve, 112 stands for a flow meter, 113 stands for an ozone generator which converts oxygen (O_2) introduced from the tube 109 into ozone (O_3) and supplies it to the tube 107 for supplying the reaction gas. Moreover, 114 stands for an evaporator containing tetraethoxysilane (TEOS), 115 stands for an evaporator containing trimethyl phosphite (TMP) as a phosphorus-containing organic compound. This evaporator is used to transport TEOS and TMP into the tube 107 by using nitrogen (N_2) supplied from the tube 110 as a carrier gas and introducing the reaction gas into the reaction furnace 101 upon mixing with O_3. Furthermore, 116 stands for a heater for heating tubes with the purpose of preventing precipitation of TEOS and TMP inside the tubes.

A silicon oxide (SiO_2) film can be formed by placing the sample 102 preheated with the heater 104 into the reaction furnace 101 of the above-described chemical vapor deposition apparatus and conducting a photochemical reaction of O_3 and TEOS. Since chemically active ozone is used in this process, the SIO_2 film can be deposited with a sufficient rate at a low temperature of less than 400°C either under a normal or a reduced pressure. Moreover, because the film is deposited under irradiation with ultraviolet radiation, a dense film can be obtained even at a low temperature of less than 400°C. For example, SiO_2 films were deposited by three processes conducted under a normal pressure and a temperature of 300°C: (1) the ozone generator was turned off (OFF) and ultraviolet radiation was produced (ON) by the low-pressure mercury lamp (photo-CVD with O_2 and TEOS), (2) the ozone generator was turned on (ON) and the low-pressure mercury lamp was turned off (OFF) (thermal CVD with O_3 and TEOS), and (3) the ozone generator was turned on (ON) and the low-pressure mercury lamp was also turned ON (the method for thin film deposition of the present embodiment). The characteristics of the obtained films were compared. As shown in Table 1, process (3) which is the process of thin film deposition of the present embodiment had the highest deposition rate and the lowest etching rate (the compactness of the film was high).

Table 1

(Film deposition temperature: 300°C)

Method for film deposition				
	Ozone generator	Low-pressure mercury lamp	Deposition rate (nm/min)	Etching rate (nm/min)
(1)	OFF	ON	10	10
(2)	ON	OFF	120	64
(3)	ON	ON	180	7
(4)	OFF	OFF	0 (no film growth)	-

A phosphorus-doped SiO_2 film (PSG film) can be deposited by adding TMP as a doping gas to O_3 and TEOS.

In the above-described example, the SiO_2 film was deposited using TEOS (organosilane) as a gaseous starting material. However, the present invention is not limited to TEOS as a gaseous starting material. For example, an inorganic insulating film can be formed by using the following materials.

Thus, a SiO_2 film can be formed by using (1) organosilane, for example, diacetoxydi(tert-butoxy)silane ($(AcO)_2Si(OtBu)_2$, DADBS) and tetramethylcyclotetrasilane ($(C_4H1_6Si_4O_4$, TMCTS)[2], as a gaseous starting material.

Alternatively, a SiO_2 film can be formed by using (2) an inorganic silane, for example, monosilane (SiH_4), disilane (Si_2H_6), and trisilane (Si_3H_8) as a gaseous starting material.

Furthermore, a silicon oxide nitride film (SiON film) can be formed by using (3) an organosilane or inorganic silane and gaseous ammonia as gaseous starting materials. In such a process, ultraviolet radiation emitted during film formation decomposes ammonia, and radicals formed in the reaction of O_3 and organic silane or inorganic silane participate in a photoreaction resulting in the film deposition.

Furthermore, a SiON film can be formed by using (4) a nitrogen-containing organosilane, for example, bis(di-(tertbutoxy)aminosilane)imido $[(t\text{-}C_4H_9O)_2SiNH_2]_2NH$, as a gaseous starting material.

Figure 2 is a cross-section of a structure obtained when a silicon oxide nitride film (SiON film) deposited by the above-described method for thin film deposition was formed as a protective film in a semiconductor integrated circuit. It is used to illustrate another embodiment of the present invention. In this figure, 201 stands for an IC chip, 202 stands for an island supporting the IC chip 201, 203 stands for a lead, 204 stands for an Al pad formed on the IC chip 201, 205 stands for a bonding wire connecting the Al pad 204 and the lead 203, 206 stands for a SiON film deposited by the method for thin film deposition, similar to the method used in the above-described embodiment and employed to protect the elements formed on the IC chip 201. The SiON film was deposited at a temperature of 380°C employing a chemical vapor deposition apparatus shown in Fig 1 and using bis(di- (tertbutoxy)aminosilane)imido as starting material. Furthermore, 207 stands for a resin forming a package.

[2] ILS Note – sic. This should probably be tetramethylcyclotetrasilane - $C_4H1_6Si_4$, or tetramethylcyclotetrasilazane $C_4H1_6Si_4O_4$.

Figure 3 illustrates the results of a moisture resistance test conducted with respect to the semiconductor devices (Fig 2) manufactured in the above-described manner. The following samples were used for the test:

(1) a semiconductor device containing no protective film 206, shown in Fig 2, (3) a device containing a SiON film (film thickness 1 micron) grown by the method of the present embodiment, and (2) a semiconductor device using a SiN film (film thickness 1 micron) formed by plasma CVD as the protective film 206. The test was conducted on 50 samples of each type. The moisture resistance test was a PCT (pressure cut test) comprising placing samples into a steam kettle at a temperature of 150°C and under a pressure of 2 atm and counting the number of defected samples. The semiconductor device using the SiON film deposited by the thin film deposition method of the present embodiment clearly had a moisture resistance superior to that of the SiN film formed by plasma CVD. Since the protective film 206 described in this embodiment was obtained without using plasma, the deposition caused no damage of the substrate. Therefore, the advantage of the invention process is that it can be widely used for the deposition of protective films on compound semiconductors, which are sensitive to substrate damages.

[Effect of the Invention]

As described above, in accordance with the present invention, an insulating film having high density and moisture resistance can be deposited at a high rate and at a low temperature on the surface of a substrate placed into a reaction furnace by introducing gaseous starting materials and ozone into the reaction furnace and irradiating the inside of the reaction furnace with ultraviolet radiation to induce a photochemical reaction of the gaseous starting materials with ozone.

4. Brief D scription of th Drawings

Figure 1 is a schematic diagram of a chemical vapor deposition apparatus illustrating an embodiment of the present invention. Figure 2 is a cross-section illustrating another embodiment of the present invention. Figure 3 is a diagram showing the results obtained in a reliability test conducted to demonstrate the effect of the present invention.

[Figure Legends]

101 - reaction furnace, 102 - sample (substrate), 103 - susceptor, 104 - heater, 105 - low-pressure mercury lamp, 106 - window for light illumination, 107 - inlet tube for reaction gas, 108 - discharge tube for reaction gas, 109 - tube for supplying gaseous oxygen, 110 - tube for supplying gaseous nitrogen, 111 - valve, 112 - flow meter, 113 - ozone generator, 114 - evaporator, 115 - evaporator, 116 - heater (for heating tubes), 201 - IC chip, 202 - island, 203 - lead, 204 - Al pad, 205 - bonding wire, 206 - SiON film (protective film), 207 - resin.

Fig 1

101 - reaction furnace, 102 - sample, 103 - susceptor, 104 - heater, 105 - low-pressure mercury lamp, 106 - window for light illumination, 107 - inlet tube for reaction gas, 108 - discharge tube for reaction gas, 109 - tube for supplying gaseous oxygen, 110 - tube for supplying gaseous nitrogen, 111 - valve, 112 - flow meter, 113 - ozone generator, 114 - evaporator, 115 - evaporator, 116 - heater

Fig 2

201 - IC chip, 202 - island, 203 - lead, 204 - Al pad, 205 - bonding wire, 206 - SiON film, 207 - resin.

Fig 3

(1) no protective film
(2) SiN film obtained by plasma COD
(3) SiON film

X-axis: PCT time (h)

Y-axis: Accumulated defect ratio (%)